

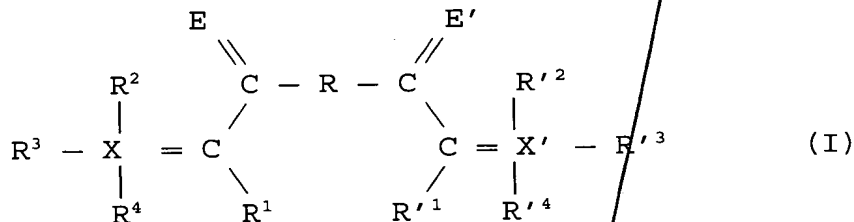
CLEAN VERSION OF CLAIMS

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## CLAIMS

46 - A catalytic system comprising:

(A) at least one ligand represented by formula (I):



where:

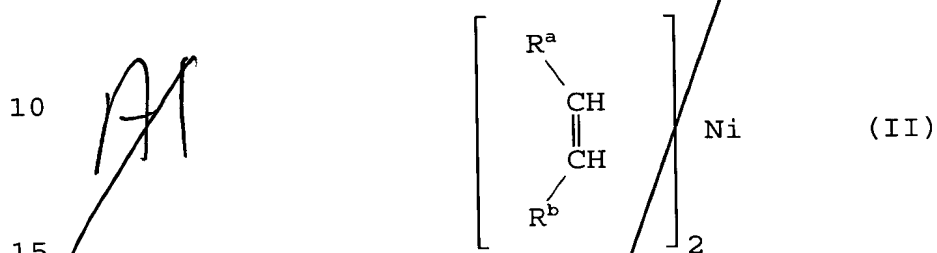
- E and E' each represent independently an oxygen or a sulfur atom;
- X and X' each represent independently a phosphorus, arsenic or antimony atom;
- the radicals R<sup>1</sup> and R'<sup>1</sup>, which are identical or different, are selected from:
  - . hydrogen;
  - . linear, branched or cyclic alkyl radicals;
  - . aryl radicals;
  - . arylalkyl radicals;
  - . alkylaryl radicals;
  - . halogens;
  - . the hydroxyl radical;
  - . alkoxide radicals;
  - .  $\begin{array}{c} \text{C} - \text{OR}' \\ || \\ \text{O} \end{array}$ , where R' represents a hydrocarbon radical which has from 1 to 15 carbon atoms;
  - . -SO<sub>3</sub>Y, where Y is selected from Li, Na, NH<sub>4</sub><sup>+</sup>, NR''<sub>4</sub><sup>+</sup>, where R'' represents a hydrocarbon radical which has from 1 to 15 carbon atoms;
- the R<sup>2</sup>, R'<sup>2</sup>, R<sup>3</sup>, R'<sup>3</sup>, R<sup>4</sup> and R'<sup>4</sup> radicals, which are identical or different, are selected from linear,

branched or cyclic alkyl radicals, and arylalkyl radicals;

- R is a divalent radical; and

(B) at least one nickel compound selected from:

5 (B1) nickel complexes with a zero oxidation state, which are represented by the general formula (II):



where  $R^a$  and  $R^b$  each represent independently a hydrogen atom, or a linear, branched or cyclic alkyl radical or aryl, arylalkyl or alkylaryl radical, which have up to 8 carbon atoms, it being also possible for  $R^a$  and  $R^b$  to form together a divalent aliphatic group of 2 to 10 carbon atoms and have up to three olefinic double bonds as the only carbon-carbon unsaturated groups;

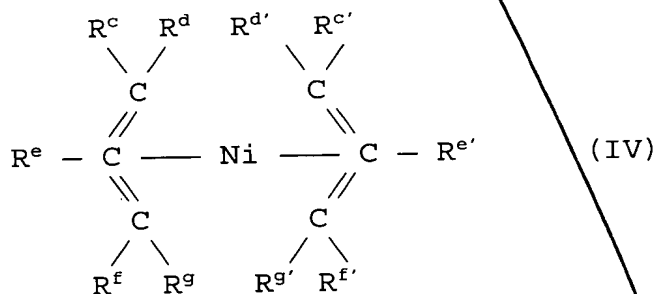
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25 (B2)  $\pi$ -allylnickels, which are represented by the formula (III):

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~~A~~

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in which:

- the radicals  $R^c$  to  $R^g$ , and  $R^{c'}$  to  $R^{g'}$ , which are identical or different, are selected from hydrogen, linear, branched or cyclic alkyl radicals and aryl, arylalkyl or alkylaryl radicals having up to 8 carbon atoms;
- the dotted lines represent the electron delocalization on the three contiguous carbon atoms;
- a radical  $R^c$  or  $R^d$  also able to form, with a radical  $R^e$  or  $R^f$  or  $R^g$ , a divalent alkene group having from 2 to 10 carbon atoms and able to have up to three olefinic double bonds;
- a radical  $R^{c'}$  or  $R^{d'}$  also able to form, with a radical  $R^{e'}$  or  $R^{f'}$  or  $R^{g'}$ , a divalent alkene group having from 2 to 10 carbon atoms and able to have up to three olefinic double bonds.

47 - The catalytic system as claimed in claim 46, wherein, in formula (I), E and E' are separated by intermediate atoms linked together by covalent or coordinate bonds.

48 - The catalytic system as claimed in claim 46, wherein, in formula (I), the minimum number of atoms between E and E' is from 3 to 40.

49 - The catalytic system as claimed in claim 46, wherein, in formula (I), R is selected from:

- . divalent hydrocarbon radicals comprising from 2 to 38 carbon atoms; and
- . the 1,1'-ferrocenylene radical which is substituted or unsubstituted.

50 - The catalytic system as claimed in claim 46, wherein the ligand of formula (I) comprises one of the following structures:

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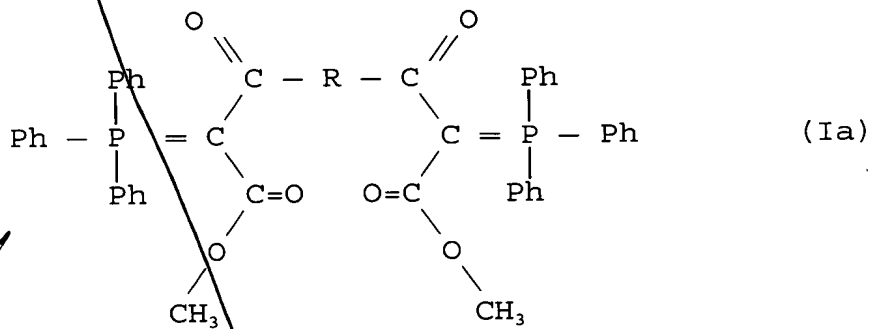
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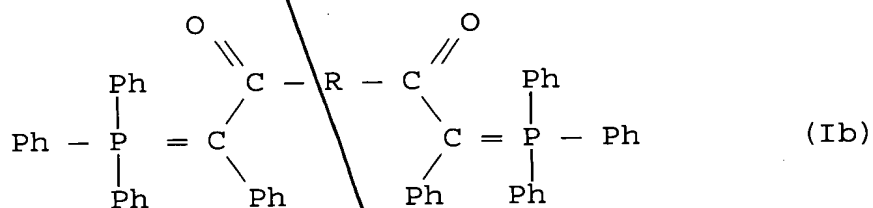
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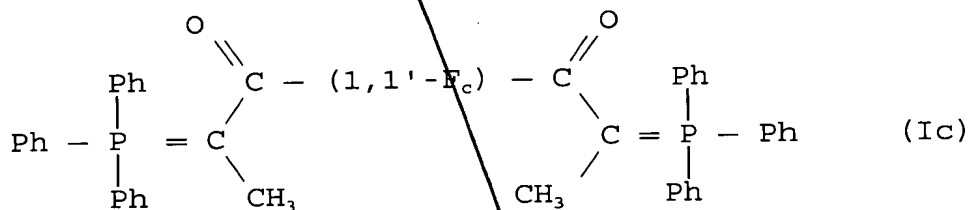
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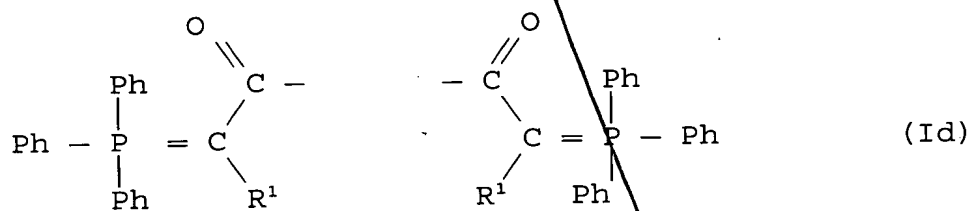
where R represents a 5,6-bicyclo[2.2.1]hept-2-ene radical;  $-(\text{CH}_2)_4-$  or  $-(\text{CH}_2)_8-$ ;



where R represents a 5,6-bicyclo[2.2.1]-hept-2-ene radical; or  $-(\text{CH}_2)_8-$ ;



where 1,1'-Fc represents a 1,1'-ferrocenylene radical; and



where  $\text{R}^1$  represents H or Ph or  $\text{SO}_3\text{Na}$  or  $-\text{C}(=\text{O})-\text{O}-\text{CH}_3$ .



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51 - The catalytic system as claimed in claim 46, wherein the nickel compound (B<sub>1</sub>) is selected from:

- AX  
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5 . bis(1,5-cyclooctadiene)nickel(0);  
  . bis(cyclooctatetraene)nickel(0); and  
  . bis(1,3,7-octatriene)nickel(0).

52 - The catalytic system as claimed in claim 46, wherein, in a nickel compound (B<sub>2</sub>) or (B<sub>3</sub>), a  $\pi$ -allyl group has from 3 to 12 carbon atoms which do not have other aliphatic unsaturated groups, except where it contains a closed cycle.

53 - The catalytic system as claimed in claim 46, wherein the nickel compound (B<sub>2</sub>) is selected from:

- 15 .  $\pi$ -allylnickel chloride;  
  .  $\pi$ -allylnickel bromide;  
  .  $\pi$ -crotylnickel chloride;  
  .  $\pi$ -methylallylnickel chloride;  
  .  $\pi$ -ethylallylnickel chloride;  
  .  $\pi$ -cyclopentylallylnickel bromide;  
  .  $\pi$ -cyclooctenylnickel chloride;  
20 .  $\pi$ -cyclooctadienylnickel chloride;  
  .  $\pi$ -cinnamylnickel bromide;  
  .  $\pi$ -phenylallylnickel chloride;  
  .  $\pi$ -cyclohexenylnickel bromide;  
  .  $\pi$ -cyclododecenylnickel chloride;  
25 .  $\pi$ -cyclododecatrienylnickel chloride;  
  .  $\pi$ -allylnickel acetate;  
  .  $\pi$ -methylallylnickel propionate;  
  .  $\pi$ -cyclooctenylnickel octoate;  
  .  $\pi$ -cyclooctenylnickel methoxylate; and  
30 .  $\pi$ -allylnickel ethoxylate.

54 - The catalytic system as claimed in claim 46, wherein the nickel compound (B<sub>3</sub>) is selected from:

- 35 . bis( $\pi$ -allyl)nickel;  
  . bis( $\pi$ -methallyl)nickel;  
  . bis( $\pi$ -cinnamyl)nickel;  
  . bis( $\pi$ -octadienyl)nickel;  
  . bis( $\pi$ -cyclohexenyl)nickel;  
  .  $\pi$ -allyl- $\pi$ -methallylnickel; and

. bis( $\pi$ -cyclooctatrienyl)nickel.

55 - The catalytic system as claimed in claim 46, wherein the components (A) and (B) are present in amounts such that the nickel-to-ligand(s) molar ratio is between 1 and 100.

56 - The catalytic system as claimed in claim 55, wherein the components (A) and (B) are present in amounts that the nickel-to-ligand(s) molar ratio is between 2 and 50.

57 - A process for the polymerization of at least one olefin in the presence of a catalytic system as defined in claim 46.

58 - The process as claimed in claim 57, wherein:

- in a first step, each of the constituents (A) and (B), which are in solution in an inert solvent, are introduced separately or simultaneously into a reactor, together with the reaction mixture; and
- in a second step, the olefin or olefins are introduced, the (co)polymerization taking place at a temperature between 0 and 300°C and at a total absolute pressure of from 1 to 200 bar.

59 - The process as claimed in claim 58, wherein the constituents (A) and (B) are introduced in a nickel-to-ligand(s) molar ratio of between 1 and 100.

60 - The process as claimed in claim 59, wherein the constituents (A) and (B) are introduced in a nickel-to-ligand(s) molar ratio of between 2 and 50.

61 - The process as claimed in claim 58, wherein the inert solvent of constituents (A) and (B) is selected from saturated aliphatic hydrocarbons, saturated alicyclic hydrocarbons, aromatic hydrocarbons and mixtures thereof.

62 - The process as claimed in claim 58, wherein the reaction mixture consists of an organic medium.

63 - The process as claimed in claim 58, wherein the reaction mixture comprises a continuous liquid aqueous phase, which comprises more than 30% water by weight.

64 - The process as claimed in claim 63, wherein the aqueous phase is the only liquid phase.

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5 - saturated aliphatic hydrocarbons, saturated alicyclic hydrocarbons, aromatic hydrocarbons and mixtures thereof; and

10 - to the extent that the polymerization conditions keep them in liquid form,  $\alpha$ -olefins, unconjugated dienes and mixtures thereof.

68 - The process as claimed in claim 67, wherein  
the dispersing agent is present at up to 10% by weight for  
15 the weight of water.

70 - The process as claimed in claim 63, wherein  
20 the polymerization medium comprises an emulsifying agent.

~~Sub C1~~ 72 - The process as claimed in claim 71, wherein  
25 the ~~emulsifying agent~~ is present at 0.01 to 5% by weight for  
the weight of water.

30            74 - The process as claimed in claim 73, wherein  
the amount of emulsifying agent is enough so that the  
polymerization takes place mainly in the micelles.

76 - The process as claimed in claim 75, wherein the polymerization mixture comprises a liquid organic phase and a cosurfactant.

76 - The process as claimed in claim 75, wherein the polymerization mixture comprises a liquid organic phase and a cosurfactant.

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79 - The process as claimed in claim 76, wherein the emulsifying agent to cosurfactant mass ratio goes from 0.5 to 2.

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82 - The process as claimed in claim 58, wherein it is carried out in an inert atmosphere.

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84 - The process as claimed in claim 83, wherein this precontacting step is carried out at a temperature between 10 and 70°C.

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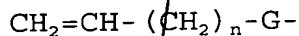
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87 - The process as claimed in claim 58, wherein the (co)polymerization is carried out at a temperature of between 25 and 200°C.

88 - The process as claimed in claim 58, wherein the (co)polymerization is carried out at a total absolute pressure of from 1 to 100 bar.

89 - The process as claimed in claim 58, wherein the olefin or olefins intended to be polymerized are introduced in gas or liquid form, with enough stirring of the polymerization medium.

90 - The process according to claim 58, wherein the olefins are selected from ethylene,  $\alpha$ -olefins, cyclic olefins and compounds of formula:



in which:

- n is an integer between 2 and 20; and
- G is a radical chosen from:

-OH;  $\text{CHOHCH}_2\text{OH}$ ; OT;  $-\text{CF}_3$ ;  $-\text{COOT}$ ;  $-\text{COOH}$ ;

$-\text{Si}(\text{OH})_3$ ;  $-\text{Si}(\text{OT})_3$ ;

T is a hydrocarbon radical having from 1 to 20 carbon atoms.

91 - The process as claimed in claim 58, wherein at least one olefin is ethylene.

92 - The process as claimed in claim 70, wherein the polymerization is carried out in the presence of an emulsifying agent, leading therefore to a latex, if necessary after a filtration step.

93 - The process as claimed in claim 92, wherein the latex is a high-density polyethylene or a medium-density polyethylene or a low-density polyethylene.

94 - The process as claimed in claim 71, wherein the emulsifying agent is present at up to 0.01 to 5% by weight, for the weight of water.

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